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A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production

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Abstract

Nano-sized TiO_2 photocatalytic water-splitting technology has great potential for low-cost, environmentally friendly solar-hydrogen production to support the future hydrogen economy. Presently, the solar-to-hydrogen energy conversion efficiency is too low for the technology to be economically sound. The main barriers are the rapid recombination of photo-generated electron/hole pairs as well as backward reaction and the poor activation of TiO_2 by visible light. In response to these deficiencies, many investigators have been conducting research with an emphasis on effective remediation methods. Some investigators studied the effects of addition of sacrificial reagents and carbonate salts to prohibit rapid recombination of electron/hole pairs and backward reactions. Other research focused on the enhancement of photocatalysis by modification of TiO_2 by means of metal loading, metal ion doping, dye sensitization, composite semiconductor, anion doping and metal ion-implantation. This paper aims to review the up-to-date development of the above-mentioned technologies applied to TiO_2 photocatalytic hydrogen production. Based on the studies reported in the literature, metal ion-implantation and dye sensitization are very effective methods to extend the activating spectrum to the visible range. Therefore, they play an important role in the development of efficient photocatalytic hydrogen production.

Keywords: Photocatalysis; Hydrogen production; Solar; Dye sensitization; Metal ion-implantation

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Contents

1. Introduction

Hydrogen is considered as an ideal fuel for the future. Hydrogen fuel can be produced from clean and renewable energy sources and, thus, its life cycle is clean and renewable. Solar and wind are the two major sources of renewable energy and they are also the promising sources for renewable hydrogen production. However, presently, renewable energy contributes only about 5% of the commercial hydrogen production primarily via water electrolysis, while other 95% hydrogen is mainly derived from fossil fuels [1]. Renewable hydrogen production is not popular yet because the cost is still high. Photovoltaic water electrolysis may become more competitive as the cost continues to decrease with the technology advancement; however, the considerable use of small band gap semiconducting materials may cause serious life cycle environmental impacts. Alternatively, photocatalytic water-splitting using TiO_2 for hydrogen production offers a promising way for clean, low-cost and environmentally friendly production of hydrogen by solar energy.

Early work of TiO_2 photoelectrochemical hydrogen production was reported by Fujishima and Honda [2]. Subsequently, scientific and engineering interests in semiconductor photocatalysis have grown significantly. Revolutionary research studies have been published in prestigious journals [2–6]. Furthermore, many review papers on semiconductor photocatalysis can be found in recent literature [7–22]. Most of the review papers emphasize semiconductor photocatalytic water/air purification [7–21], but very few of them are related to photocatalytic hydrogen production [22]. Both photocatalytic water/air purification and photocatalytic hydrogen production require essential photogeneration of hole/electron pairs. However, their utilization of holes/electrons as well as the system processing are different. In photocatalytic water/air purification, valence band (VB) holes are the key elements that induce decomposition of contaminants.

The conduction band (CB) level is insignificant. On the other hand, when photocatalysis is applied to perform water-splitting for production of hydrogen, the reducing CB

electrons become important as their role is to reduce protons to hydrogen molecules. The CB level should be more negative than the hydrogen evolution level (E_{H_2/H_2O}) to initiate hydrogen production. The above factors imply that photocatalytic water/air purification conditions may not be applicable to photocatalytic hydrogen production. Review and discussion of the state-of-the-art of photocatalytic hydrogen production technologies are thus beneficial.

Ashokkumar [22] wrote an overview on semiconductor particulate systems for hydrogen production. Potentials of various photocatalysts for hydrogen production, such as CdS, TiO_2 and SiC, were discussed. Additionally, different catalyst modification methods, such as noble metal loading, addition of sacrificial reagent and dye sensitization were evaluated. Since then, a number of new technologies have been developed, including anion doping and metal ion-implantation. This paper aims to give a comprehensive review on the recent development of photocatalytic hydrogen production using photocatalyst TiO_2. Compared with other photocatalysts, TiO_2 is much more promising as it is stable, non-corrosive, environmentally friendly, abundant and cost effective. Based on recent research works, the enhancement methods for photocatalytic hydrogen production are reviewed and summarized. Some works on water/air purification applications as well as on photocatalysts other than TiO_2 are also discussed for comparison and better understanding.

2. Mechanisms of semiconductor photocatalytic water-splitting or hydrogen production

The electronic structure of a semiconductor plays a key role in semiconductor photocatalysis. Unlike a conductor, a semiconductor consists of VB and CB. Energy difference between these two levels is said to be the band gap (E_g). Without excitation, both the electrons and holes are in valence band. When semiconductors are excited by photons with energy equal to or higher than their band gap energy level, electrons receive energy from the photons and are thus promoted from VB to CB if the energy gain is higher than the band gap energy level. For semiconductor TiO_2, the reaction is expressed as:

$$TiO_2 \overset{hv}{\rightarrow} e^-_{TiO_2} + h^+_{TiO_2} \tag{1}$$

The photo-generated electrons and holes can recombine in bulk or on surface of the semiconductor within a very short time, releasing energy in the form of heat or photons. Electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidize the reactants adsorbed by the semiconductor. The reduction and oxidation reactions are the basic mechanisms of photocatalytic hydrogen production and photocatalytic water/air purification, respectively. Both surface adsorption as well as photocatalytic reactions can be enhanced by nano-sized semiconductors as more reactive surface area is available.

For hydrogen production, the CB level should be more negative than hydrogen production level (E_{H_2/H_2O}) while the VB should be more positive than water oxidation level (E_{O_2/H_2O}) for efficient oxygen production from water by photocatalysis.

The photocatalytic hydrogen production by TiO_2 is shown in Fig. 1. Theoretically, all types of semiconductors that satisfy the above-mentioned requirements can be used as photocatalysts for hydrogen production. However, most of the semiconductors, such as CdS and SiC, that cause photocorrosion, are not suitable for water-splitting. Having

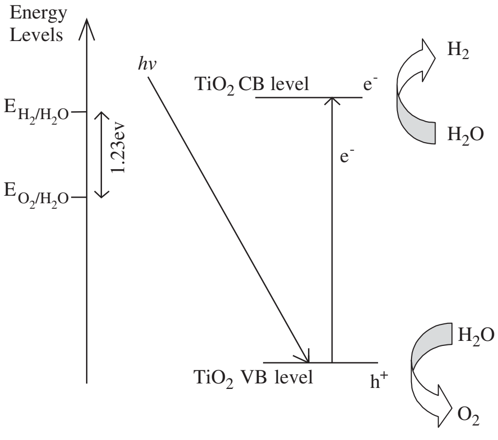


Fig. 1. Mechanism of TiO_2 photocatalytic water-splitting for hydrogen production.

strong catalytic activity, high chemical stability and long lifetime of electron/hole pairs, TiO_2 is the most widely used photocatalyst. Presently, the energy conversion efficiency from solar to hydrogen by TiO_2 photocatalytic water-splitting is still low, mainly due to the following reasons:

(1) Recombination of photo-generated electron/hole pairs: CB electrons can recombine with VB holes very quickly and release energy in the form of unproductive heat or photons;
(2) Fast backward reaction: Decomposition of water into hydrogen and oxygen is an energy increasing process, thus backward reaction (recombination of hydrogen and oxygen into water) easily proceeds;
(3) Inability to utilize visible light: The band gap of TiO_2 is about 3.2 eV and only UV light can be utilized for hydrogen production. Since the UV light only accounts for about 4% of the solar radiation energy while the visible light contributes about 50%, the inability to utilize visible light limits the efficiency of solar photocatalytic hydrogen production.

In order to resolve the above listed problems and make solar photocatalytic hydrogen production feasible, continuous efforts have been made to promote the photocatalytic activity and enhance the visible light response. Addition of electron donors (hole scavengers), addition of carbonate salts, noble metal loading, metal ion doping, anion doping, dye sensitization, composite semiconductors, metal ion-implantation etc., were investigated and some of them have been proved to be useful to enhance hydrogen production. The above listed techniques influencing H_2 production have been grouped under two broad classifications, such as 'chemical additives' and 'photocatalyst modification techniques' The fundamental mechanisms, current development and potential of these methods for hydrogen production are discussed in the following sections.

3. Chemical additives for H_2 production enhancement

3.1. Addition of electron donors

Due to rapid recombination of photo-generated CB electrons and VB holes, it is difficult to achieve water-splitting for hydrogen production using TiO_2 photocatalyst in distilled water. Adding electron donors (sacrificial reagents or hole scavengers) to react irreversibly with the photo-generated VB holes can enhance the photocatalytic electron/hole separation resulting in higher quantum efficiency. Since electron donors are consumed in photocatalytic reaction, continual addition of electron donors is required to sustain hydrogen production.

Organic compounds (hydrocarbons) are widely used as electron donors for photocatalytic hydrogen production as they can be oxidized by VB holes. The remaining strong reducing CB electrons can reduce protons to hydrogen molecules. EDTA, methanol, ethanol, CN^-, lactic acid and formaldehyde have been tested and proved to be effective to enhance hydrogen production [23–30]. Nada et al. [29] carried out a qualitative investigation to study the effects of different electron donors on hydrogen production. The rankings in terms of the degree of hydrogen production enhancement capability were found to be: EDTA > methanol > ethanol > lactic acid. It should be noted that the decomposition of these hydrocarbons could also contribute to a higher hydrogen yield since hydrogen is one of their decomposed products.

Photocatalytic decomposition of pollutants and photocatalytic production of clean hydrogen fuel can take place simultaneously when the pollutants are acted as electron donors. Li et al. [26] reported enhanced photocatalytic hydrogen production in single component systems and mixture systems of pollutants (oxalic acid, formic acid and formaldehyde) acting as electron donors. Decomposition of the electron donors was reported to be consistent with hydrogen production. Furthermore, unlike a single component system, a mixture system involved competition of adsorption on the photocatalyst surface. Despite the limited work on using pollutants as electron donors, the encouraging results shows the promise of the integration of pollutant decomposition and hydrogen production.

Other inorganic ions, such as S^{2-}/SO_3^{2-} [31], Ce^{4+}/Ce^{3+} [32] and IO_3^-/I^- [33–35] were used as sacrificial reagents for hydrogen production. When CdS is used as photocatalyst for water-splitting hydrogen production, photocorrosion occurs as follows:

$$CdS + 2h^+ \rightarrow Cd^{2+} + S \tag{2}$$

Serving as a sacrificial reagent, S^{2-} can react with 2 holes to form S. The aqueous SO_3^{2-} added can dissolve S into $S_2O_3^{2-}$ in order to prevent any detrimental deposition of S onto CdS. Therefore, photocorrosion of CdS is prevented. In another system using inorganic ions, I^- (electron donor) and IO_3^- (electron acceptor) work as a pair of redox mediators. Two photocatalysts were employed to produce H_2 and O_2 under the mediation of I^- and IO_3^-, respectively [33–35]. For hydrogen production on the photocatalyst with more negative CB level, I^- can scavenge holes and, thus, CB electrons are available to reduce protons to hydrogen molecules. For oxygen production on the photocatalyst with more positive VB level, IO_3^- can react with CB electrons to form I^- and, thus, VB holes can oxidize water to oxygen. In this system, photocatalytic water-splitting produces both hydrogen and oxygen without consumption of the sacrificial reagent, as illustrated

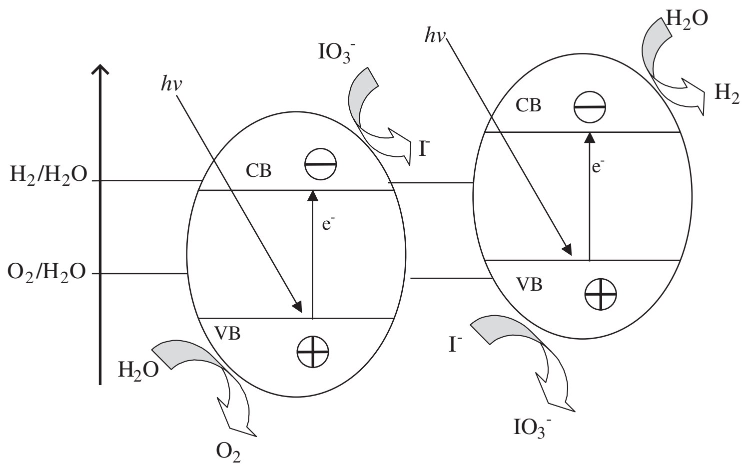


Fig. 2. Photocatalytic hydrogen production under the mediation of I^-/IO_3^-.

in Fig. 2. The rates of hydrogen production employing these redox mediators are presented in Table 1 [33]. As rutile has unique selectivity in oxidation, oxygen molecules are evolved. For comparison, IO_3^- anions are produced on the surface of anatase. Therefore, the combination of anatase and rutile shows a higher hydrogen production rate under the mediation of $I^- = IO_3^-$ pairs. Similarly, Ce^{4+}/Ce^{3+} and Fe^{3+}/Fe^{2+} pairs are also effective for water-splitting hydrogen production.

3.2. Addition of carbonate salts to suppress backward reaction

Sayama et al. [36–42] reported that addition of carbonate salts could significantly enhance hydrogen and oxygen production stoichiometrically. Addition of Na_2CO_3 was found to be effective for enhancement of hydrogen and oxygen production using Pt loaded TiO_2 (Pt-TiO_2) [36]. Later, various semiconductor photocatalysts including TiO_2, Ta_2O_5 and ZrO_2 were tested and it was found that the presence of Na_2CO_3 was very beneficial for hydrogen and oxygen production for all the photocatalysts tested [37]. The Infrared (IR) study revealed that the surface of Pt-TiO_2 catalyst was covered by many types of carbonate species, such as HCO_3^-, $CO_3^{\cdot-}$, $HCO_3^{\cdot}$ and $C_2O_6^{2-}$. These carbonate species were formed through the following reactions:

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{3}$$

$$HCO_3^- + h^+ \rightarrow HCO_3^{\cdot} \tag{4}$$

$$HCO_3^{\cdot} \rightleftharpoons H^+ + CO_3^{\cdot-} \tag{5}$$

$$CO_3^{\cdot-} \rightarrow C_2O_6^{2-} \tag{6}$$

Therefore, photo-generated holes were consumed by reacting with carbonate species to form carbonate radicals, which is beneficial for photo-excited electron/hole separation.

Table 1
Photocatalytic hydrogen production rates of TiO_2 suspended in aqueous solution containing 40 mmol of NaI (pH 11) [33]

Photocatalyst	Surface area	Gas production rate[a] ($\mu mol\ h^{-1}$)	
	($m^2\ g^{-1}$)	H_2	O_2
Pt-TiO_2-A1	320	20[b]	Tr. (trace)
Pt-TiO_2-A2	48	6[b]	Tr.
TiO_2-A1	320	0	0
TiO_2-A2	48	0	0
Pt-TiO_2-R1	40	Tr.	0
Pt-TiO_2-R2	2	Tr.	0
TiO_2-R1	40	0	0
TiO_2-R2	2	0	0
Pt-TiO_2-A1+TiO_2-R1		125	62
Pt-TiO_2-A1+TiO_2-R2		180	90
Pt-TiO_2-A2+TiO_2-R1		8	4
Pt-TiO_2-A2+TiO_2-R2		18	9
Pt-TiO_2-R1+TiO_2-A1		<1	Tr.
Pt-TiO_2-A1+TiO_2-A2		Tr.	Tr.
Without catalyst		0	0

Catalyst: 0.5 g (in case of mixture 0.25 + 0.25 g), water 400 ml, NaI 40 mmol, Pyrex reactor of inner irradiation type, high pressure Hg lamp (400 W).
[a]Rate in steady state.
[b]Initial rate: TiO_2-A1 (anatase, 320 $m^2\ g^{-1}$, Ishihara ST-01); TiO_2-A2 (anatase, 48 $m^2\ g^{-1}$, prepared by hydrolysis of titanium tetraproproxide); TiO_2-R1 (rutile, 40 $m^2\ g^{-1}$, Ishihara TTO-55N); TiO_2-R2 (rutile, 2 $m^2\ g^{-1}$, Toho titanium HT 0210).

On the other hand, peroxycarbonates were easily decomposed into O_2 and CO_2,

$$C_2O_6^{2-} + 2h^+ \rightarrow O_2 + 2CO_2 \quad (7)$$

The evolution of CO_2 and O_2 could promote desorption of O_2 from the photocatalyst surface and thus could minimize the formation of H_2O through the backward reaction of H_2 and O_2. Then desorbed CO_2 soon was dissolved and converted into HCO_3^-, in turn effecting H_2 production.

Although the results are very encouraging (Table 2) [38], the mechanism has yet not been fully understood. Since CO_3^{2-} was the main factor responsible for higher H_2 photocatalytic production, addition of the same amount of Na_2CO_3 and K_2CO_3 should exhibit comparable photocatalytic activity. However, when Pt-TiO_2 was used as photocatalyst, addition of Na_2CO_3 was more effective than addition of K_2CO_3 in terms of hydrogen production (Table 3) [42]. The reason to the above phenomenon is still unknown.

Addition of iodide was also found to be advantageous for hydrogen production [43]. Iodide anion (I^-) in a suspension can be adsorbed preferentially onto Pt surface, forming an iodine layer. The iodine layer can thus suppress backward reaction of H_2 and O_2 to form H_2O. Accordingly, the production of hydrogen and oxygen was enhanced very significantly. However, adding too much carbonate salt or iodide anion beyond optimum level could reduce the beneficial effects, since these species adsorbed onto the catalyst surface could decrease light harvesting [38].

Table 2
Rate of photocatalytic production of H_2 and O_2 from ZrO_2 aqueous suspensions containing several additives [38]

Additives	Rates of gas production (μmol h^{-1})	
	H_2	O_2
None	72	36
NaOH	242	120
Na_3PO_4	228	113
Na_2CO_3	378	190
$NaBO_2$	164	84
Na_2HPO_4	129	65
$NaHCO_3$	607	319
Na_2SO_4	112	56
NaCl	91	48
HCl	46	19
H_3PO_4	65	33
H_2SO_4	85	39

Note: ZrO_2 1.0 g; water 350 ml; inner irradiated quartz cell; high pressure Hg lamp (400 W). Concentration of Na^+ and H^+ was 0.012 mol per 350 ml of water.

Table 3
Rate of photocatalytic production of H_2 and O_2 over a Pt/TiO_2 suspension with salt additives [42]

Additives	Additive (mol)	Gas evolution Rate (μmol h^{-1})[a]		
		H_2	O_2	pH
None	—	1	0	7.9
Na_2CO_3	0.10	3	1	10.9
	0.38	316	158	11.0
	0.76	568	287	11.0
	1.14	39	13	11.0
K_2CO_3	0.38	5	1	11.5
	1.45	20	10	11.8
$NaHCO_3$	0.10	4	2	8.4
Li_2CO_3	0.06	13	3	10.8
NaOH	0.76	5	0	13.3

Note: Pt(0.3 wt%)-TiO_2: 0.3 g, water: 350 ml, an inner irradiation quartz reactor, high pressure Hg lamp (400 W).
[a]Rate at steady state.

4. Photocatalyst modification techniques to enhance H_2 production

4.1. Noble metal loading

Noble metals, including Pt, Au, Pd, Rh, Ni, Cu and Ag, have been reported to be very effective for enhancement of TiO_2 photocatalysis [28,44–60]. As the Fermi levels of these noble metals are lower than that of TiO_2, photo-excited electrons can be transferred from CB to metal particles deposited on the surface of TiO_2, while photo-generated VB holes remain on the TiO_2. These activities greatly reduce the possibility of electron-hole recombination, resulting in efficient separation and stronger photocatalytic reactions.

Anpo and Takeuchi [61] employed Electron Spin Resonance (ESR) signals to investigate electron transfer from TiO_2 to Pt particles. It was found that Ti^{3+} signals increased with irradiation time and the loading of Pt reduced the amount of Ti^{3+}. This observation indicates the occurrence of electron transfer from TiO_2 to Pt particles. As electrons accumulate on the noble metal particles, their Fermi levels shift closer to the conduction band of TiO_2 [50,52,53], resulting in more negative energy levels. This is beneficial for water-splitting hydrogen production. Furthermore, smaller metal particles deposited on TiO_2 surface exhibit more negative Fermi level shift [50]. Accumulated electrons on metal particles can then be transferred to protons adsorbed on the surface and further reduce the protons to hydrogen molecules. Therefore, noble metals with suitable work function can help electron transfer, leading to higher photocatalytic activity.

Bamwenda et al. [45] compared hydrogen production from water-ethanol solution using Au-loaded TiO_2 and Pt-loaded TiO_2 as photocatalysts. Different metal particle deposition methods, such as deposition–precipitation, impregnation and photodeposition were also tested. It was found that loading of Pt worked better than loading of Au. Furthermore, Au loading prepared by photodeposition worked better than deposition–precipitation and impregnation. The variations might be explained by the better contact with TiO_2 active sites for photodeposition method. However, Pt-loaded TiO_2 was found to be less sensitive to the preparation methods. Sakthivel et al. [46] investigated photooxidation of acid green 16 using Pt, Au and Pd-loaded TiO_2 as photocatalysts. Optimal loading was observed in their experiments. Since, as mentioned earlier, too much metal particle deposition might reduce photon absorption by TiO_2 and might also become electron-hole recombination centers, resulting in lower efficiency. Loadings of Pt and Au were more effective than loading of Pd because of suitable electron affinity and work function of Pt and Au [46].

It should be noted that although the loading of noble metal can reduce recombination to some extent, hydrogen production from pure water-splitting is difficult to achieve, because: (i) recombination cannot be completely eliminated; (ii) backward reaction of H_2 and O_2 to form H_2O is thermodynamically favorable. Therefore, as discussed in the previous sections, electron donors or carbonate salts as well as other mediators are required to avoid the above listed problems. Since Pt is very expensive, more research is needed to identify low-cost metals with acceptable enhancement of photocatalytic activity. For example, Dhanalakshimi et al. [62] investigated dye sensitised hydrogen production. When Pt/TiO_2 and Cu/TiO_2 were used as photocatalysts, enhanced hydrogen production was observed and the effect of Cu loading was almost comparable to Pt loading. Unlike dye sensitization, Wu and Lee [28] deposited Cu particles on TiO_2 surface for hydrogen production from methanol solution. At the optimal loading of Cu, hydrogen production rate was enhanced as much as 10 times higher. Other low-cost metals, such as Ni and Ag [60], were also found to be effective for photocatalytic activity enhancement. These low-cost but effective metals are expected to be promising materials to improve photocatalytic activities of TiO_2 for practical applications.

4.2. *Ion doping*

4.2.1. *Metal ion doping*

Transitional metal ion doping and rare earth metal ion doping have been extensively investigated for enhancing the TiO_2 photocatalytic activities [63–78]. Choi et al. [63] carried out a systematic investigation to study the photoreactivity of 21 metal ions doped

into TiO_2. It was found that doping of metal ions could expand the photo-response of TiO_2 into visible spectrum. As metal ions are incorporated into the TiO_2 lattice, impurity energy levels in the band gap of TiO_2 are formed, as indicated below:

$$M^{n+} + hv \rightarrow M^{(n+1)+} + e^-_{ch} \tag{8}$$

$$M^{n+} + hv \rightarrow M^{(n-1)+} + h^-_{vb} \tag{9}$$

where M and M^{n+} represent metal and the metal ion dopant, respectively.

Furthermore, electron (hole) transfer between metal ions and TiO_2 can alter electron-hole recombination as:

$$\text{Electron trap}: M^{n+} + e^-_{cb} \rightarrow M^{(n-1)+} \tag{10}$$

$$\text{Hole trap}: M^{n+} + h^+_{vb} \rightarrow M^{(n-1)-} \tag{11}$$

The energy level of $M^{n+}/M^{(n-1)+}$ should be less negative than that of the CB edge of TiO_2, while the energy level of $M^{n+}/M^{(n+1)+}$ should be less positive than that of the VB edge of TiO_2. For photocatalytic reactions, carrier transferring is as important as carrier trapping. Only if the trapped electron and hole are transferred to the surface, photocatalytic reactions can occur. Therefore, metal ions should be doped near the surface of TiO_2 particles for a better charge transferring. In case of deep doping, metal ions likely behave as recombination centers, since electron/hole transferring to the interface is more difficult. Furthermore, there exists an optimum concentration of doped metal ion, above which the photocatalytic activity decreases due to the increase in recombination. Among the 21 metal ions studied, Fe, Mo, Ru, Os, Re, V, and Rh ions can increase photocatalytic activity, while dopants Co and Al ions cause detrimental effects [63]. The different effects of metal ions result from their abilities to trap and transfer electrons/holes. For example, Cu and Fe ions can trap not only electrons but also holes, and the impurity energy levels introduced are near to CB as well as VB edges of TiO_2. Therefore, doping of either Cu or Fe ions could be recommended for enhancement of photocatalytic activity [63,64,72,74,75].

A qualitative analysis in investigating the effects of doping transitional metal ions (Cr, Mn, Fe, Co, Ni, and Cu) on photocatalytic activity of TiO_2 was carried out by Wu et al. [69]. Acetic acid photocatalytic oxidation was employed to evaluate the effects of different metal ion doping. As Cu, Mn and Fe ions can trap both electrons and holes, doping of these metal ions may work better than doping of Cr, Co and Ni ions, as the latter metal ions can only trap one type of charge carrier. Xu et al. [67] compared photocatalytic activities of different rare earth metal ions (La, Ce, Er, Pr, Gd, Nd and Sm) doped into TiO_2. Enhanced photocatalytic activities and red shift of photo-response were observed at certain doping content. Dopant Gd ions were found to be most effective in enhancing the photocatalytic activity due to its highest ability to transfer charge carriers to the interface (surface of TiO_2).

Hameed et al. [66,91] studied photocatalytic water-splitting for hydrogen production using transitional metal ions (Fe, Co, Ni, Cu and Zn) doped WO_3 under UV laser irradiation. The CB edge of WO_3 was less negative than E_{H_2/H_2O}. Therefore, WO_3 under irradiation in water could not reduce protons to hydrogen molecules. However, when transitional metal ions were on the surface of WO_3, transitional metal oxides were formed, which could further act as composite semiconductor photocatalysts. As FeO, CoO, NiO

and Cu_2O had more negative CB levels than E_{H_2/H_2O}, the CB electrons were able to reduce protons. Unlike the above four metal oxides, ZnO could not capture electrons from CB of WO_3. Therefore, doping of Zn was found to be less effective than other metal ions. Doping of 1% and 10% Ni ions exhibited the highest hydrogen production rate, which might be partly attributed to mechano-catalytic water-splitting hydrogen production, since magnetic stirrer was employed [91]. It was reported that when NiO or Cu_2O was used with magnetic stirrer, hydrogen could be produced by water-splitting even in the dark, known as mechano-catalytic reaction [79–90]. Unlike the above study, Wu et al. [69] reported that doping of Cu and Fe ions in TiO_2 was more effective for acetic acid oxidation degradation than doping of Ni ions. The discrepancy could be explained by different forms of doping. In Wu et al.'s study, metal ions were doped in the lattice of TiO_2 particles, while in Hameed et al.'s work, metal ions were deposited on the surface of WO_3 in a form of metal oxide, resulting in composite semiconductors.

Peng et al. [30] investigated the effect of Be ion doped TiO_2 on photocatalytic hydrogen production in the presence of electron donors (ethanol). It was found that doping the metal ions near the surface was beneficial for charge carrier transferring, while deep doping led to poor performance. The findings were consistent with Choi's results [63]. Furthermore, doping contents and preparation methods could also affect photocatalytic hydrogen production. Under optimal condition of Be ion doping into TiO_2, hydrogen production was found to be 75% higher than that of un-doped TiO_2.

Extensive research on metal ion doping method for enhancement of TiO_2 photocatalytic activities has been carried out especially for water/air cleaning applications. Organic compounds adsorbed by the photocatalysts are decomposed mainly by the VB holes and radicals induced by holes. Therefore, the mechanism involved in transferring these photo-generated holes to the interface is of paramount importance. On the other hand, for photocatalytic hydrogen production, the transfer of CB electrons to the interface and their energy levels are the most important factors that affect the hydrogen production rate. Hence, the results based on water/air cleaning applications cannot be directly applied to hydrogen production. Besides, the TiO_2 photocatalytic effect is very sensitive to the metal ion doping methods, doping content and depth. Therefore, a systematic, comparative investigation is needed in order to characterize photocatalytic hydrogen production enhanced by metal ion doping.

4.2.2. Anion doping

The use of anion doping to improve hydrogen production under visible light is rather a new method with few investigations reported in open literature. Doping of anions (N, F, C, S etc.) in TiO_2 crystalline could shift its photo-response into visible spectrum [3,92–102]. Unlike metal ions (cations), anions less likely form recombination centers and, therefore, are more effective to enhance the photocatalytic activity. Asahi et al. [3] determined the substitutional doping contents of C, N, F, P and S for O in anatase TiO_2. It was found that mixing of *p* states of N with 2*p* of O could shifts VB edge upwards to narrow down the band gap of TiO_2. Although doping of S had resulted in a similar band gap narrowing, the ionic radius of S was reported to be too large to be incorporated into the lattice of TiO_2. Dopants C and P were found to be less effective as the introduced states were so deep that photo-generated charge carriers were difficult to be transferred to the surface of the catalyst. The nitrogen doped TiO_2 thin film was prepared by sputtering TiO_2 in an N_2 (40%)/Ar gas mixture, followed by annealing at 550 °C in N_2 for about 4 h. Nitrogen

doped TiO_2 powder was also prepared by treating TiO_2 in NH_3(67%)/Ar at 600 °C for 3 h. The N-doped TiO_2 was reported to be effective for methylene blue decomposition under visible light ($\lambda > 400$ nm).

Additionally, it was reported by Umebayashi et al. [92] that S doped TiO_2 could be prepared by oxidation annealing of TiS_2. Annealed at 600 °C, TiS_2 was partly changed to anatase TiO_2. The residual S atoms in the anatase TiO_2 formed S-doped TiO_2 by Ti-S bonds. Band structures of the S-doped TiO_2 were calculated using the super cell approach. It was found that when TiO_2 was doped with S, the mixing of S 3*p* states with the VB of TiO_2 increased the width of VB, resulting in band gap narrowing. Since the band gap narrowing was caused by VB upward shifting, the CB remained unchanged. Therefore, the S-doped TiO_2 should be able to reduce protons for hydrogen production under visible light. On the other hand, the upward shift of VB may reduce the oxidation ability under visible light. Ohno et al. developed a new method to prepare S-doped TiO_2 powder [93]. Titanium isopropoxide was mixed with thiourea in ethanol and stirred. After subsequent evaporation, aging and calcination, S-doped TiO_2 powder was obtained. The S ions were incorporated to replace some of the Ti atoms in the form of S^{4+}. The photocatalytic activity of S-doped TiO_2 was then evaluated by photodecomposition of 2-propanol and methylene blue. It was reported that S-doped TiO_2 worked better than pure TiO_2 under visible light irradiation. Although the VB was shifted upwards, the oxidation ability was found to be still high. Other anions, such as C and F ion have also been investigated and found to be able to expand photo-response in visible spectrum [94–96]. N-doped TiO_2 have been extensively investigated. The reported methods to dope N are heating of titanium hydroxide and urea [97], reactive DC magnetron sputtering [98–101], nitriding of anatase TiO_2 with alkylammonium salts [102] and treating TiO_2 powder in NH_3 (80%)/Ar gas flow at 550 °C [103].

Similar to S-doping, N-doping also caused a VB upward shift resulting in a narrow band gap and less oxidating holes. Mrowetz et al. [103] reported that N-doped TiO_2 was unable to oxidize $HCOO^-$. However, for hydrogen production, electrons are responsible for reducing protons and the ability of oxidation does not affect the performance, since the VB level of TiO_2 is far more positive than oxygen evolution energy level. As such CB remains almost unchanged after N-doping, being at a more negative than hydrogen production energy level. This throws a possibility that N-doped TiO_2 should be able to reduce protons for hydrogen production, although no such research has been reported yet. Under visible light irradiation, electrons can be promoted from energy levels in the band gap formed by nitrogen doping to CB. However, electron-hole recombination possibility of N-doped TiO_2 was reported to be higher than undoped TiO_2 [99]. For efficient photocatalytic reaction, coupling with other technologies, such as noble metal loading or electron donor addition, is necessary.

4.3. Sensitization

4.3.1. Dye sensitization

Dye sensitization is widely used to utilize visible light for energy conversion. Some dyes having redox property and visible light sensitivity can be used in solar cells as well as photocatalytic systems [24,62,104–107]. Under illumination by visible light, the excited dyes can inject electrons to CB of semiconductors to initiate the catalytic reactions as illustrated in Fig. 3. Even without semiconductors, some dyes, for example safranine

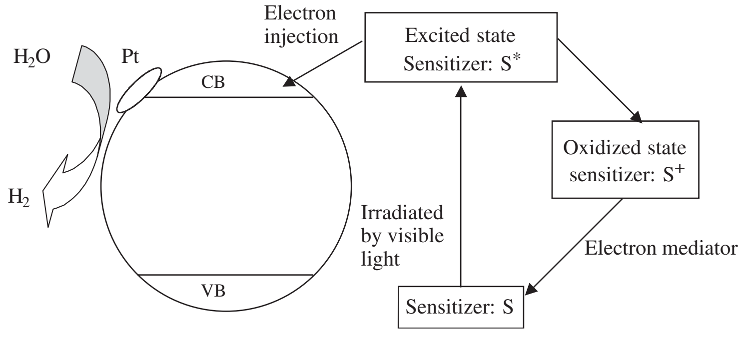


Fig. 3. Mechanism of dye-sensitized photocatalytic hydrogen production under visible light irradiation.

O/EDTA and T/EDTA, are able to absorb visible light and produce electrons as reducing agents strong enough to produce hydrogen [108]. Nevertheless, without semiconductors acting as efficient charge separators, the rate of hydrogen production merely by dyes is very low.

High hydrogen production rate can be obtained by efficient absorption of visible light and efficient transfer of electrons from excited dyes to the CB of TiO_2. Some of the frequently used dyes together with their absorption wavelength maxima are listed in Table 4 [104]. The CB electrons can then be transferred to noble metal particles (Pt) loaded on the surface to initiate water reduction. In order to regenerate dyes, redox systems or sacrificial agents, such as I_3^-/I^- pair [109] and EDTA [105], can be added to the solution to sustain the reaction cycle. The excitation, electron injection and dye regeneration can be expressed as follows [110]:

$$\text{dye} \stackrel{hv}{\rightarrow} \text{dye}^* \tag{12}$$

$$\text{dye}^* \stackrel{TiO_2}{\rightarrow} \text{dye}^+ + e^- \tag{13}$$

$$\text{dye}^+ + e^- \rightarrow \text{dye} \tag{14}$$

To obtain a higher efficiency in converting absorbed light into direct electrical energy (for solar cells) or hydrogen energy, fast electron injection and slow backward reaction are required. Based on the literature on electron/hole recombination of dyes, the recombination times were found to be mostly in the order of nanoseconds to microseconds, sometimes in milliseconds [111–113], while the electron injection times were in the order of femtoseconds [112,114,115]. The fast electron injection and slow backward reaction make dye-sensitized semiconductors feasible for energy conversion.

Dhanalakshmi et al. [62] carried out a parametric investigation to study the effect of using $[Ru(dcpy)_2(dpq)]^{2+}$ as a dye sensitizer on photocatalytic hydrogen production from water, under visible light irradiation. It was found that hydrogen production rate was enhanced by adsorbing dye molecules to the TiO_2. The optimal combination of catalyst and Pt loading was found. Additional Pt or dye loading beyond the optimal values, hydrogen production rate did not further increase. This phenomenon indicated that only

Table 4
Absorption wavelength maxima (λ_{max}) dyes [103]

Dye	Class	λ_{max} (nm)
Thionine (TH^{+})	Thiazines	596
Toluidine blue (Tb^{+})	Hiazines	630
Methylene blue (MB)	Thiazines	665
New methylene blue	Thiazines	650
Azure A	Thiazines	635
Azure B	Thiazines	647
Azure C	Thiazines	620
Phenosafranin (PSF)	Phenazines	520
Safranin-O (Saf-O/SO)	Phenazines	520
Safranin-T (Saf-T/ST)	Phenazines	520
Neutral red (NR)	Phenazines	534
Fluorescein	Xanthenes	490
Erythrosin	Xanthenes	530
Erythrosin B	Xanthenes	525
Rhodamin B (Rh. B)	Xanthenes	551
Rose Bengal	Xanthenes	550
Pyronine Y (PY)	Xanthenes	545
Eosin	Xanthenes	514
Rhodamin 6G	Xanthenes	524
Acridine orange (AO)	Acridines	492
Proflavin (PF)	Acridines	444
Acridine yellow (AY)	Acridines	442
Fusion	Triphenyl methane derivatives	545
Crystal violet	Triphenyl methane derivatives	578
Malachite green	Triphenyl methane derivatives	625
Methyl violet	Triphenyl methane derivatives	580

dye molecules adsorbed on the surface of TiO_2 could effectively inject electrons into TiO_2 for water reduction.

Gurunathan et al. [24] investigated the effects of different dyes on photocatalytic hydrogen production by SnO_2 with and without a sacrificial agent, such as EDTA. The band gap of SnO_2 is 3.5 eV and, hence, it could not be excited by visible light. After SnO_2 was sensitized by dyes, hydrogen production was observed under visible light illumination. Qualitatively, the ranking of dyes in terms of the degree of enhancement of hydrogen production rate was found in the following order: eosin blue > rose bengal > $Ru(bpy)_3^{2+}$ > rhodamine$B \approx$ acriflavin > fluorescein. However, based on the structures and properties of these dyes, a general conclusion could not be drawn. For example, rhodamine B showed the longest absorption wavelength maxima together with more negative reduction potential (−0.545 V) than CB level (−0.34 V) of SnO_2, but it did not increase hydrogen production rate significantly. Therefore, the difference in their electron injection characteristics may be the reason for the variation in hydrogen production rates. However, comparison of electron injection characteristics among these dyes was not available. Further research work is thus required to compare dynamics of charge excitation, recombination and electron injection of different dyes to gain a better understanding of the mechanisms behind the phenomena.

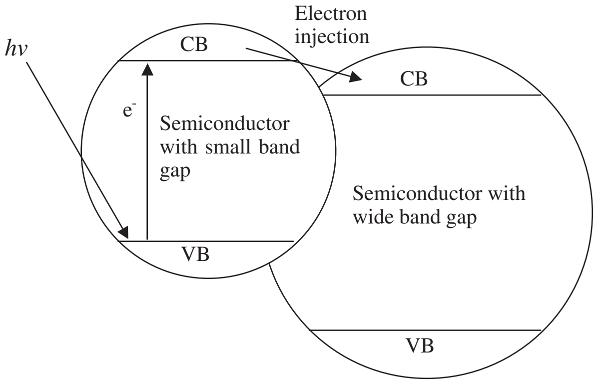


Fig. 4. Electron injection in composite semiconductors.

4.3.2. Composite semiconductors

Semiconductor composition (coupling) is another method to utilize visible light for hydrogen production. When a large band gap semiconductor is coupled with a small band gap semiconductor with a more negative CB level, CB electrons can be injected from the small band gap semiconductor to the large band gap semiconductor. Thus, a wide electron-hole separation is achieved as shown in Fig. 4. The process is similar to dye sensitization. The difference is that electrons are injected from one semiconductor to another semiconductor, rather than from excited dye to semiconductor. Successful coupling of the two semiconductors for photocatalytic water-splitting hydrogen production under visible light irradiation can be achieved when the following conditions are met: (i) semiconductors should be photocorrosion free, (ii) the small band gap semiconductor should be able to be excited by visible light, (iii) the CB of the small band gap semiconductor should be more negative than that of the large band gap semiconductor, (iv) the CB of the large band gap semiconductor should be more negative than E_{H_2/H_2O} and (v) electron injection should be fast as well as efficient.

It has been reported that coupling of CdS (band gap 2.4 eV) with SnO_2 (band gap 3.5 eV) could produce hydrogen under visible irradiation [24]. Electrons excited to the CB (−0.76 eV) of CdS are injected to the CB (−0.34 eV) of SnO_2 in less than 20 ps, resulting in wide electron-hole separation. Sacrificial agent, EDTA, has to be added to scavenge VB holes on CdS; otherwise, photocorrosion of CdS would occur. Doong et al. [116] coupled CdS with TiO_2 for 2-chlorophenol degradation under UV irradiation. In their study, both CdS and TiO_2 could be excited. The combination of the two semiconductors showed better photocatalytic activity due to better charge separation. The CB electrons of CdS are injected to the CB of TiO_2, while the VB holes in TiO_2 are injected to the VB of CdS. Kang et al. [117] employed CdS-TiO_2 composite semiconductor for 4-CP photodegradation and found that coupling of CdS with TiO_2 was more effective than CdS and TiO_2 used separately.

Besides the above-mentioned environmental applications, composite semiconductor of CdS-TiO_2 can be applied to produce hydrogen since the CB of TiO_2 is more negative than E_{H_2/H_2O}. So et al. [118] conducted photocatalytic hydrogen production using CdS-TiO_2 composite semiconductors. Photocorrosion of CdS was prevented by

addition of Na_2S. Optical absorption spectra analysis showed that CdS-TiO_2 could absorb photons with wavelength up to 520 nm. Under visible light illumination (Xe lamp), CdS-TiO_2 composite semiconductors produced hydrogen at a higher rate than CdS and TiO_2 used separately.

De et al. [119] conducted solar photocatalytic hydrogen production using CdS-ZnS composite semiconductor. Photocorrosion was inhibited by addition of Na_2S/Na_2SO_3 solution. Under solar irradiation, addition of n-Si enhanced hydrogen production. This was due to the smaller band gap of n-Si together with its more negative CB. When exposed to solar radiation with wavelength longer than 520 nm, electrons were excited from the VB of n-Si to the CB of n-Si and then transferred to the CB of CdS sequentially, resulting in a higher solar radiation utilization. Similar work employing CdS-ZnS composite semiconductor for solar hydrogen production was reported by Koca and Sahin [31]. They prepared their photocatalyst CdS-ZnS by coprecipatating of hot solutions to improve the hydrogen production rate. This may be due to better contact between CdS and ZnS particles, which could in turn improve the transfer of electrons.

Besides coupling with small band gap semiconductors, TiO_2 coupled with a large band gap semiconductor has also been investigated and proven to be more efficient under UV irradiation. Keller and Garin [120] observed that photocatalytic oxidation of methylethylketone (MEK) was increased by coupling TiO_2 with WO_3 (2.7 eV band gap) and SiC (3.0 eV band gap). As the CB of SiC was more negative, electron transfer to the CB of TiO_2 could be more efficient. On the other hand, the CB of WO_3 was less negative than that of TiO_2, and thus electrons were transferred from the CB of TiO_2 to WO_3, resulting in a wide electron-hole separation. These composite semiconductors were found to be more effective than TiO_2 for MEK oxidation due to efficient charge separation. However, although WO_3 coupling with TiO_2 could enhance photocatalytic oxidation, it could not reduce protons, since the CB of WO_3 was not negative enough. Comparatively, the electrons transferred from the CB of SiC to the CB of TiO_2 were more negative than E_{H_2/H_2O}; therefore, SiC coupling was suitable for hydrogen production under UV illumination. Meanwhile, Nguyen et al. [121] studied the effect of electronic characteristics of TiO_2-SiO_2 and RuS_2/TiO_2-SiO_2 on hydrogen production. They observed that the coupled TiO_2-SiO_2 semiconductor showed more negative CB than TiO_2. When further coupled with RuS_2, electrons could be transferred to the CB of RuS_2 (−0.6 eV), accomplishing reduction of protons to hydrogen molecules.

Tennakone and Bandara [122] attached dye-sensitized SnO_2 nanocrystallites (10–15 nm) to platinized ZnO (about 600 nm) particles for photocatalytic hydrogen production from water, in the presence of hole scavenger (ethanol). It was found that although the CB of SnO_2 was lower (less negative) than that of ZnO, electrons from excited dyes could be transferred to ZnO via SnO_2 without relaxation to the CB energy level of SnO_2. It was observed that electron transfer from dye to semiconductor particle (Fig. 5) was very fast. The hydrogen production rate of the coupled Pt/ZnO/SnO_2/dye was found to be much higher (0.92 ml) than Pt/ZnO/dye (0.04 ml) and other combinations of these materials. Such high hydrogen production rate could be achieved by wide charge separation with SnO_2. The successful electron transfer was possible only when the particle size of SnO_2 was small. Otherwise, electrons might be relaxed to the CB of SnO_2, inhibiting hydrogen production. Platinum loading on the surface of ZnO was also found to be very effective for hydrogen production enhancement. It is expected that suitable coupling of different modification methods can contribute to a higher hydrogen production rate.

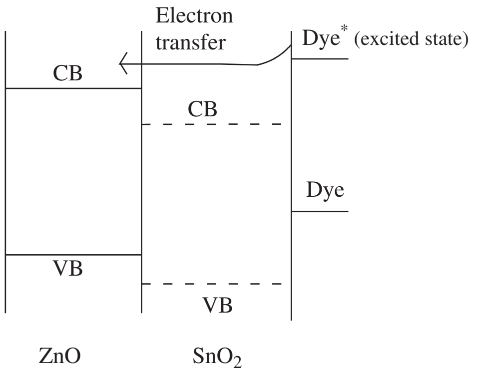


Fig. 5. Energy level diagram indicating the band positions of SnO_2, ZnO as well as the ground and excited state levels of the dye.

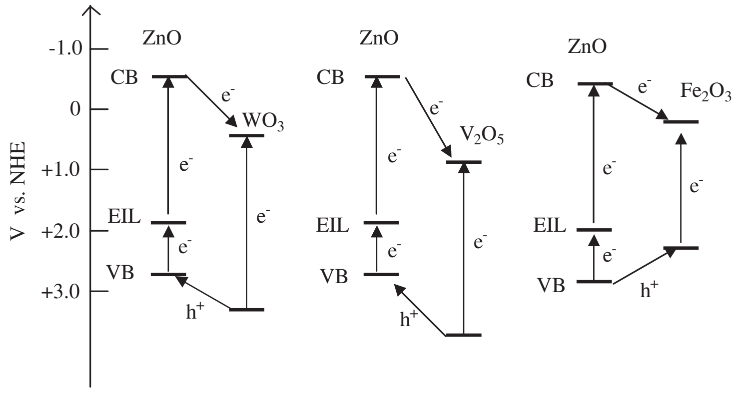


Fig. 6. Schematics of charge separation for N-doped MO_x-ZnO composite semiconductors (M represents W, V and Fe).

Recently, Li et al. [123] developed a novel photocatalyst by coupling nitrogen doping and composite semiconductors as shown in Fig. 6. Nitrogen-doped ZnO was coupled with WO_3, V_2O_5 and Fe_2O_3 for acetaldehyde decomposition under visible light. By doping of nitrogen, ZnO could respond with visible spectrum. Unlike coupling with WO_3 and V_2O_5, coupling with Fe_2O_3 caused the photocatalytic activity to deteriorate since Fe_2O_3 served as both an electron sink and a hole sink. Although N-doped ZnO-WO_3 and ZnO-V_2O_5 work better under visible light irradiation for acetaldehyde decomposition, they are not suitable for hydrogen production since the CB of both WO_3 and V_2O_5 are not negative enough. It is expected that a N-doped composite semiconductor with CB level to be more negative than E_{H_2/H_2O}, such as SiC-TiO_2, may serve as an efficient photocatalyst for hydrogen production under visible light irradiation.

4.4. Metal ion-implantation

Metal ion-implantation was recently reported to be an effective method to modify semiconductor electronic structures to improve visible light response [124–134]. When

TiO_2 is bombarded with high-energy transitional metal ions (accelerated by high voltage), these high-energy ions are injected into the lattice and interact with TiO_2. This process modifies TiO_2 electronic structure and shifts its photo-response to the visible region (up to 600 nm). Presently metal ion implanted TiO_2 is believed to be the most effective photocatalyst for solar energy utilization and is in general referred as the 'second generation photocatalyst.'

Takeuchi et al. [124] implanted Cr-ion into TiO_2 thin film for NO decomposition under visible light irradiation. The TiO_2 thin film was prepared by ionized cluster beam (ICB) method. In this method, metal Ti was heated up to 2000 K and the Ti vapor was introduced into a high vacuum chamber in the presence of O_2 to produce TiO_2 thin film [125].

The main advantages of ICB (dry methods) over wet preparation methods are: (i) contamination with impurities can be prevented as this process is usually carried out in a high vacuum chamber, (ii) high crystalline TiO_2 can be obtained as calcination is avoided and (iii) the properties of thin film, such as thickness of the coating, can be controlled. The TiO_2 thin film was then treated by Cr-ion-implantation. The UV-visible absorption spectra showed that Cr-ion implanted TiO_2 thin film can absorb visible light and the extent of red shift increased with increasing amount of Cr-ion implanted. It was found that Cr-ion implanted TiO_2 worked efficiently in photocatalytic decomposition of NO under both UV and visible light irradiation. It indicated that metal ion-implantation did not work as recombination center. Comparatively, TiO_2 with chemically doped Cr ions could not decompose NO under visible light irradiation ($\lambda > 450$ nm). It implied that metal ion-implantation modified the electronic structure of TiO_2 in a way different from chemical doping that formed impurity energy levels in the band gap of TiO_2.

Studies of ion-implantation of TiO_2 have been conducted for V-ions, Mn-ions, Ni-ions, Ar-ions, Mg-ions, Ti-ions and Fe-ions [126–134]. Except Ar-ions, Mg-ions and Ti-ions, implantation of all other metal ions resulted in red shift. The qualitative effectiveness of red shift was observed to be in the following order: V > Cr > Mn > Fe > Ni. It was also reported that only when implantation was followed by calcinations in an O_2 atmosphere at around 723–823 K, red shift could be realized. Both optimal depth and amount of metal ions implanted were obtained experimentally. Through molecular orbital calculations [126], metal ions (V^{5+}, V^{4+}, V^{3+}) were found to substitute with Ti^{4+} ions, octahedrally coordinated in the lattice position of TiO_2. Therefore, the mixing of Ti(d) orbital of Ti-oxide with metal(d) orbital of the implanted metal ions leads to band gap narrowing.

From the preliminary investigations, it has been shown that metal ion-implantation is comparatively very effective for red shift. Further, in comparison with composite semiconductor and dye sensitization in which electron mediator and sacrificial agents are required to sustain the reaction cycles, metal ion-implantation is advantageous as no electron mediator is required. Although water-splitting hydrogen production using metal ion-implantation has not yet been reported, the present development has demonstrated the potential for efficient solar photocatalytic hydrogen production.

5. Conclusions

A number of modification techniques and chemical additives have been developed in recent years to improve photocatalytic activity of TiO_2 under visible light irradiation. Applications include the promising photocatalytic water splitting capability for hydrogen

production. Presently, the hydrogen production rate obtained is low due to quick charge recombination, quick backward reaction and inability to utilize visible light efficiently. Addition of electron donors (hole scavengers) can enhance hydrogen production by reacting with VB holes irreversibly to prohibit charge recombination. In order to achieve sustainable hydrogen production, continual addition of electron donors is required. Using waste organic compounds as electron donors could accomplish both tasks of hydrogen production as well as waste treatment simultaneously. Addition of carbonate salts or other electron mediators can prevent backward reaction and thereby enhance the hydrogen production rate.

Loading of metal particles on the surface of TiO_2 can inhibit charge recombination. The most frequently used metal is Pt, which is very efficient but expensive. Lower cost alternative metals, such as Cu, Ni and Ag, should be tested for possible substitution. Metal ion doping on TiO_2 can expand its photo-response to visible region through formation of impurity energy levels. However, the effect of red shift is negligible and doped ions tend to become recombination centers. Therefore, the benefit of metal ion doping is limited. Qualitatively, anion doping, such as nitrogen doping and sulfur doping, is more effective than metal ion doping for red shift. Dye sensitization and composite semiconductor are the two promising surface modification methods to expand light-response of TiO_2 to visible region. Excited dyes and small band gap semiconductors can inject electrons to the CB of large band gap semiconductors, resulting in efficient charge separation and high photocatalytic efficiency. In order to sustain the reaction cycles, electron sacrificial agents or redox mediators is required. The energy levels and charge transfer should be considered carefully when designing such photocatalytic hydrogen production system. Metal ion-implantation is another promising modification technique for red shift of TiO_2. Visible light with wavelength up to 600 nm can be utilized by metal ion-implanted TiO_2 photocatalysts. Unlike metal ion doping in which the ions usually work as recombination centers, metal ion-implantation does not form impurity energy level and shows high photocatalytic activity under both UV and visible light irradiation.

To ensure efficient hydrogen production, coupling different techniques, is essential. For example, when dye-sensitized TiO_2 loaded by noble metal is coupled with redox mediator, sustainable hydrogen production can be realized under solar irradiation. Furthermore, no simulation model has been developed for photocatalytic hydrogen production, although some models have been developed for photocatalytic water/gas purification or dye-sensitized solar cells. The modeling work is thus required for better understanding of the hydrogen production mechanism as well as for designing efficient photoreactor. It is anticipated that the low cost, environmentally friendly photocatalytic water-splitting for hydrogen production will play an important role in the hydrogen production and contribute much to the coming hydrogen economy.

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